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A PROGRAM TO DEVELOP A HIGH-ENERGY DENSITY PRIMARY BATTERY WITH A MINIMUM OF 200 WATT HOURS PER POUND OF TOTAL BATTERY WEIGHT

by

William E. Elliott, Shih-liang Hsu, and Warren L. Towle

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FIRST QUARTERLY REPORT
July – September, 1964

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SUMMARY

The purpose of this work is to develop a primary battery capable of delivering a minimum of 200 watt-hours per pound of total battery weight.

The emphasis in the first quarter has been placed on the study of the behavior of nonaqueous electrolytes. Of the numerous solutions tested, the solvents acetonitrile and N-nitrosodimethylamine produced solutions with the highest conductances. For example, one-molal KPF_6 in acetonitrile and one-molal di-n-butylammonium in N-nitrosodimethylamine gave conductance values of 3.3×10^{-2} and 2.7×10^{-2} ohm^{-1} cm^{-1}, respectively. The best solutes were those possessing alkali metal or quarternary ammonium cations and hexafluorophosphate, hexafluoroarsenate or hexafluoroantimonate anions. The exploratory tests using mixed solvents, solutes prepared metathetically, diluents to control viscosity, and low melting fused salts all have demonstrated the feasibility of the concepts involved. Temperature coefficients for a number of nonaqueous solutions have also been determined and are generally less than two per cent per degree Centigrade. Appendix I, page V-1, compares methods of expressing concentration as related to conductance comparisons.

Finally, the preliminary electrochemical tests demonstrated the feasibility of discharging lithium anodes in an ethylene carbonate-propylene carbonate solution.

INTRODUCTION

The present work is the extension of contract NAS 3-2790 for which the objective is that of developing a primary battery with an energy density of at least 200 watt-hours per pound of total battery weight.

Thus far, the emphasis has been placed upon the continued development of aprotic electrolytes of high conductivity in recognition of the importance of the latter property for good battery performance. In this respect, the experimental work has been directed toward obtaining extensive data on the conductivities of a variety of nonaqueous systems with a view toward clarification of the basic factors influencing conductivity in such systems.

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ABSTRACT

A number of new solvents and solutes have been tested during this period. Solvents which produced solutions with the highest conductances were acetonitrile and N-nitrosodimethylamine. The best solutes were those with alkali metal or quaternary ammonium cations and with hexafluorophosphates, hexafluoroantimonates, or hexafluoroarsenates as the anions. Exploratory tests with mixed solvents, metathetical solute preparations, diluents to control viscosity, and with low melting fused salts have all demonstrated feasibility of the concepts involved. Temperature coefficients for a number of systems were found to be less than 2% per degree Centigrade. Finally, we have demonstrated that ethylene carbonate-propylene carbonate solutions can be used to discharge lithium anodes satisfactorily.

I. OVERALL PROGRESS

I. OVERALL PROGRESS

The experimental work in the first quarter has been primarily directed toward the development of highly conductive nonaqueous electrolytes. Some preliminary electrochemical tests were also performed.

A. Electrolytes.

1. Evaluation of New Solvents.

The following solvents were selected to study the influence of solvent structure and other solvent properties on the behavior of their solutions.

a. Acetonitrile [AN] CH_3CN

b. Ethylene Carbonate [EC] 

c. Mesityl Oxide [MO] $(CH_3)_2C = CHCOCH_3$

d. N-Nitrosodimethylamine [NDA] $(CH_3)_2NNO$

e. Tetramethyldiaminomethane [TMDAM] $(CH_3)_2NCH_2N(CH_3)_2$

f. Tetramethylethylenediamine [TMEDA] $(CH_3)_2N(CH_2)_2N(CH_3)_2$

g. Trifluoroacetic Anhydride [TFAA] $(CF_3CO)_2O$

Some of the solvent properties are presented in Table I (page IV-1). The stability test results for two prospective anode materials (Li and Mg) in several of the above solvents are tabulated in Table II (page IV-2).

AN has been used as an electrolyte solvent by other workers for some time. Although it appears that this solvent is unstable in the presence of lithium, it was chosen for the present investigation to study the solvating power of the nitrile group. It was also felt that the low viscosity of this solvent would have a beneficial effect upon the conductivity of solutions.

EC was expected to perform better than propylene carbonate (PC) as a solvent since EC and PC are chemically alike and EC has a much higher dielectric constant. However, EC is a solid at normal room temperature (m.p. = 36°C). We elected to mix EC and PC to obtain mixed solvents with melting points below normal room temperature. The viscosities of the mixed solvents were found to be independent of the relative EC-PC concentration. The results are presented in Table III (page IV-3), together with the dielectric constants.

Mesityl oxide has a structure which includes a carbonyl group and a carbon-carbon double bond, both of which might be expected to have some effect on solvent power. It has a dielectric constant of 15. However, the hydrogen atoms attached to the alpha-carbon atoms should make mesityl oxide protic. Stability test results indicated that magnesium is stable in mesityl oxide and no evolution of hydrogen was observed over a period of six days. Since in general the solvent did not yield high conductance solutions, no other stability tests were run.

NDA was selected as a solvent to study the complexing power of its nitroso group and the influence on the conductance of its solutions. Its dielectric constant (53) is considerably higher than that of the two promising solvents (ϵ = 37) -- dimethylformamide (DMF) and dimethyl cyanamide (DMC) -- which have been studied in our previous work. The viscosity of NDA at 25°C was found to be 0.865 centipoise which is comparable to that of DMF (0.813 c.p.) and DMC (0.670 c.p.). These properties of NDA are favorable in obtaining high conductance NDA solutions.

TMDAM and TMEDA possess no carbonyl groups but each has two amino nitrogens for possible complex formation with the solutes. These compounds should enable us to evaluate the effect of the carbonyl group on the solvent power by comparing TMDAM and TMEDA with the previously tested tetramethylurea (TMU) which has a structure of $(CH_3)_2NCON(CH_3)_2$.

Trifluoroacetic anhydride has completely fluorinated alpha-carbon atoms and is therefore aprotic. However, it was found to have a low dielectric constant of about 2. It was felt that the effect of the high density of carbonyl groups (two per molecule) on complexing and hence on conductance might dominate the low dielectric constant effect. Stability test results show that magnesium itself was apparently stable in TFAA and

its oxide film reacted with TFAA and formed a white insoluble solid, probably magnesium trifluoroacetate.

2. Qualitative Screening.*

The seven new solvents mentioned above were used in the conductance screening tests with some of the more promising solutes tested previously in other solvents. A number of new compounds, including tributyltin chloride and triphenyltin chloride, were added to the list of solutes. The solvents, dimethylformamide (DMF), dimethyl cyanamide (DMC) and PC were also used in the conductance screening tests.

All the results of the screening tests are presented in Table IV (pages IV-4 through IV-9). It was observed that:

a. The conductances of the AN solutions of two hexafluorophosphates exceeded 3×10^{-2} ohm^{-1} cm^{-1} at one-molal concentrations.

b. Most of the solutes were soluble in NDA to one-molal concentration and yielded conductances in excess of 2×10^{-2} ohm^{-1} cm^{-1}. These values are slightly higher than the conductances of the corresponding DMF and DMC solutions.

c. The saturated PC solutions of some of the quaternary ammonium salts had conductance values of 1.0×10^{-2} ohm^{-1} cm^{-1} -- by far the best among all of the PC systems.

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* See Appendix I, page V-1, for a discussion of the significance of methods of expressing concentration as related to the comparison of the conductances of solutions.

The EC-PC solutions showed somewhat higher conductances than those of the corresponding PC solutions. It appeared that the solubilities of the solutes in PC and in EC-PC did not differ significantly, whether expressed as molality or molarity.

d. Most of the solutes had limited solubilities (much less than one-molal) in MO, TFAA, TMEDA, and TMDAM. The highest obtained conductance among these saturated solutions was 1.68×10^{-3} ohm^{-1} cm^{-1} for N-phenyl N,N,N-trimethylammonium hexafluorophosphate in MO.

e. The solutions of the organotin chlorides in DMF and DMC had poor conductance values ($< 2 \times 10^{-4}$ ohm^{-1} cm^{-1}).

3. Conductance vs. Concentration.*

The quantitative relationship between conductance and concentration was determined for the following systems (Table V, pages IV-10 through IV-22):

** a. KPF_6-DMC

b. $NaSbF_6$-DMC

** c. $(n\text{-}C_3H_7)_4NPF_6$-DMC (Tetra-n-propylammonium hexafluorophosphate)

** d. $K_3Cr(SCN)_6$-DMF

** e. $NaB(C_6H_5)_4$-DMF (Sodium tetraphenylboron)

f. $NaSbF_6$-DMF

g. KPF_6-NDA

** h. $O\langle CH_2CH_2\rangle NH_2PF_6$ (Morpholinium hexafluorophosphate)

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* See Appendix I, page V-1.
** With viscosity data.

i. $(n\text{-}C_4H_9)_2NH_2AsF_6$-NDA (Di-n-butylammonium hexafluoroarsenate)

j. $AlCl_3$-(80% EC + 20% PC)

** k. $KAsF_6$-(80% EC + 20% PC)

** l. $O\begin{smallmatrix}\diagup CH_2CH_2 \diagdown \\ \diagdown CH_2CH_2 \diagup\end{smallmatrix} NH_2PF_6$(80% EC + 20% PC) (Morpholinium hexafluorophosphate)

It was observed that maximum conductance existed at a concentration of less than two-molal and in most cases viscosity increased drastically as the concentration exceeded that of maximum conductance. System "h" above exhibited a maximum conductance plateau over a wide concentration range and the viscosity change was not very steep in this concentration range (1 to 2 molal).

4. Conductance vs. Temperature Tests.

The temperature coefficients of conductances of a number of the solutions possessing high conductances were determined. the results are graphically presented in Figure 1 (page IV-23). It was found that:

a. The temperature coefficient was higher for the higher concentration solutions than that for the corresponding lower concentration solutions.

b. The temperature coefficient was higher near room temperature than that at a higher temperature.

c. Most of the measured temperature coefficients were lower than two per cent per degree centigrade as indicated by the slope of the dotted line shown in Figure 1.

** With viscosity data.

5. Mixed Solvents. *

a. EC-PC. The reasons for using EC-PC mixed solvents have been discussed in a previous section. KPF_6 was used as the solute. The conductances and viscosities were determined for the one-molal KPF_6 solutions as a function of relative EC-PC concentrations (Figure 2, page IV-24). It was found that the one-molal KPF_6 in 80% EC + 20% PC solution has a higher conductance (about 43% higher) and a lower viscosity (even lower on a constant molarity basis) than that of the corresponding PC solution, whereas the dielectric constant of 80% EC + 20% PC is about 35% higher than that of PC.

b. DMF-TMU and DMF-PC. Previous test results indicate that TMU may be a better complexing agent than DMF, which in turn is better than PC where KPF_6 was used as the solute. PC has a higher dielectric constant than DMF whereas that of DMF is higher than that of TMU. It was felt that upon proper mixing of two of these solvents, an improved solvent might result and its KPF_6 solution might exhibit improved conductance over that of the corresponding single solvent solutions. The experiments were carried out at 0.1 mole fraction of KPF_6 for two mixed solvents -- DMF-TMU and DMF-PC. (These curves would not differ significantly on a molarity scale.) The conductance results are graphically presented in Figure 3 (page IV-25) and Figure 4 (page IV-26). No enhancement of conductance was observed in either case.

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* See Appendix I, page V-1.

c. DMF-TMDAM. TMDAM has a low viscosity (0.39 centipoise) and was tested as a diluent to be added to KPF_6-DMF solutions. It was found that as the concentration of KPF_6 was increased, the liquid separated into two layers. The highest obtained conductance before phase separation was only 1.2×10^{-2} ohm^{-1} cm^{-1}.

6. Metathesis.*

Since not all of the desired solutes were available commercially for studying the ion size effect, metathetic preparations were attempted in several cases.

a. $(CH_3)_4NSbF_6$-DMF. This solution was prepared by reacting $(CH_3)_4NCl$ with $NaSbF_6$ in DMF to form insoluble NaCl and soluble $(CH_3)_4NSbF_6$. Chemical analysis* showed that the reaction was about 90% complete and the resulting solution was 0.90 molal with respect to $(CH_3)_4NSbF_6$ and 0.10 molal with respect to $NaSbF_6$. It exhibited a conductance of 2.65×10^{-2} ohm^{-1} cm^{-1} (28°C) which is the highest conductance among the one-molal solutions prepared with DMF.

b. $(CH_3)_4NAsF_6$-DMF. This solution was prepared by reacting $(CH_3)_4NCl$ with $KAsF_6$ in DMF to form insoluble KCl and soluble $(CH_3)_4NAsF_6$. Chemical analysis$^{\Delta}$ showed that the final solution was saturated with respect to $(CH_3)_4NAsF_6$

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* See Appendix I, page V-1.

$^{\Delta}$ All the analyses of K and Na were performed by means of flame photometer and the analysis of Cl was performed by means of Volhard titration.

at 0.76 molal and 0.21 molal with respect to $KAsF_6$. It had a conductance of 2.17×10^{-2} ohm^{-1} cm^{-1} (31°C).

c. $\underline{(CH_3)_4NPF_6\text{-DMF}}$. This solution was prepared by reacting $(CH_3)_4NCl$ with KPF_6 in DMF to form soluble $(CH_3)_4NPF_6$ and insoluble KCl. Chemical analysis* shows that the resulting solution was saturated with respect to $(CH_3)_4NPF_6$ at 0.57 molal and less than 0.02 molal with respect to KPF_6. It had a conductance of 1.34×10^{-2} ohm^{-1} cm^{-1} at 27°C as compared to the previously reported value of 1.09×10^{-2} ohm^{-1} cm^{-1} at 26°C for a saturated $(CH_3)_4NPF_6$-DMF solution by using commercial $(CH_3)_4NPF_6$.

The following conclusions may be drawn from the results of the above mentioned experiments:

1. The solubility of $(CH_3)_4N\underline{Sb}F_6$ in DMF is greater than that of $(CH_3)_4N\underline{As}F_6$ in DMF which in turn is greater than that of $(CH_3)_4N\underline{P}F_6$ in DMF.
2. The conductance at the concentration of the above DMF solution of $(CH_3)_4N\underline{Sb}F_6$ is higher than that of $(CH_3)_4N\underline{As}F_6$ which in turn is greater than that of $(CH_3)_4N\underline{P}F_6$.

d. $\underline{R_3SnPF_6\text{-DMF}}$. The attempts of preparing the organo tin hexafluorophosphates metathetically were unsuccessful since neither $(n\text{-}C_4H_9)_3SnCl$ nor $(C_6H_5)_3SnCl$ appeared to react with KPF_6 in DMF to form the desired products.

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* All the analyses of K and Na were performed by means of flame photometer and the analysis of Cl was performed by means of Volhard titration.

7. Exploratory Tests.

Trifluoroacetic anhydride and oxamide each has two carbonyl groups per molecule and were chosen to study the complexing power of multifunctional carbonyl group compounds. Preliminary tests were performed by adding the complexing agent to the solutions of DMC and DMF of KPF_6 and $MgCl_2$. The conductance was recorded after each incremental addition of the complexing agent. No favorable effect on conductance was observed except with TFAA addition to $MgCl_2$-DMF solutions wherein a somewhat higher conductance (about 35%) was obtained. Further work will be performed to determine the real cause of the increase in conductance.

Tripropylamine (TPA) is a basic solvent and was chosen to study the effect of increasing the basicity of the solvent on the conductance of solutions. Preliminary tests were performed by adding TPA to some of the solutions possessing promising conductances. Some favorable results were obtained. However, further data are required for the complete interpretation of these experiments.

8. Preparation of Low-Melting Complexes.

A KPF_6·TMU complex was prepared and extracted from TMU. It has a melting point of about 36°C. This complex was then dissolved in solvents such as DMF. The preliminary conductance

results indicate that this $KPF_6 \cdot TMU$ complex is no better than KPF_6 itself as a solute. Further tests are in progress to study the behavior of this complex.

B. Electrochemical Tests.

The electrochemical behavior of a lithium anode was studied in an electrolyte* consisting of LiCl and $AlCl_3$ in an EC-PC solvent. An open circuit potential of 3.1 volts against a silver-silver chloride reference electrode in the same electrolyte was obtained. Preliminary test results showed that the discharge voltage of the lithium anode at 2 ma/cm^2 was steady, and above 2.6 volts for about three hours. This demonstrates the feasibility of using a lithium anode in a high EC content EC-PC electrolyte which is more conducting than the corresponding PC electrolyte.

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* LiCl = 0.50 g-mol
$AlCl_3$ = 0.75 g-mol
EC = 800 g
PC = 200 g

II. CURRENT PROBLEMS

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Recently we were unable to obtain some of the solute chemicals from commercial sources with consistent quality. As a result, some of the quantitative tests on nonaqueous electrolytes were interrupted. This difficulty is expected to be overcome shortly.

III. WORK TO BE PERFORMED

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A. Next Quarter:

1. Continued qualitative and quantitative study of new electrolyte systems.
2. Continued study of low melting complexes.
3. Continued study of compatibility and electrochemical behavior of electrode materials in the high conductance electrolytes.
4. Evaluation of new solvents.

B. Next Month:

1. Continued qualitative screening of electrolyte systems.
2. Continued study of low melting KPF_6-tetramethylurea complex.
3. Evaluation of the following new solvents:
   a. Methylene chloride
   b. Trifluoroacetophenone
   c. S-ethyltrifluorothioacetate
   d. N-acetylmorpholine
   e. N-2-hydroxyethyl-N,N'-ethylenebisformamide
   f. N-[2-(2-hydroxyethoxy)-ethyl]-formamide

IV. TEST RESULTS

TABLE I. PROPERTIES OF SOLVENTS

	M.W.	M.P.(°C)	B.P.(°C)	Dielectric Constant	Density (g/c.c.)	Viscosity (Centipoises)
Acetonitrile	41.05	-45	81.6	37.5 (20°C)	0.783 (20°C)	0.345 (25°C)
Ethylene Carbonate	88	36	248	89.1 (40°C)	1.322 (39°C)	2.0 (40°C)
Mesityl Oxide	98.14	-59	129	15	0.854	---
N-nitrosodimethylamine	74.08	---	152-3	53 (20°C)	* 0.9995(25°C)	* 0.865 (25°C)
N,N,N',N' Tetramethyldiaminomethane	102.18	---	83	---	* 0.741	* 0.39
N,N,N',N' Tetramethylethylenediamine	116.21	---	120	---	* 0.770	* 0.71
Trifluoroacetic Anhydride	210.04	---	40	* 2.1	* 1.469	---

* Determined experimentally at room temperature.

TABLE II. STABILITY TESTS

	Gm. of Sample				
	Before Exposure	After Exposure	Specific Conductance (ohm^{-1} cm^{-1})	Exposure Time (Hrs.)	Visual Observations
			a. In Dimethyl Cyanamide		
Blank			8.40×10^{-6} (29.5°C)	0	---
			9.50×10^{-6} (24.5°C)	115	---
Mg	0.1196	0.1183	1.17×10^{-5} (24.5°C)	115	No Apparent Reaction
			b. In Mesityl Oxide		
Blank			5.80×10^{-7} (28°C)	0	---
			9.01×10^{-7} (30°C)	144	---
Mg			2.31×10^{-6} (27°C)	144	No Visible Change
			c. In Trifluoroacetic Anhydride		
Blank			2.52×10^{-9} (27°C)	0	---
			6.60×10^{-8} (26°C)	144	---
Mg			5.30×10^{-8} (28°C)	144	Apparently Unstable - Formed White Solid
			d. In Acetonitrile		
Blank			1.58×10^{-6} (27°C)	92	---
Li			7.26×10^{-4} (28°C)	92	Gassing
Mg			1.93×10^{-6} (27°C)	92	No Apparent Reaction

TABLE III. PROPERTIES OF ETHYLENE CARBONATE-PROPYLENE CARBONATE MIXED SOLVENT

Solvent Composition			
Weight % EC	Weight % PC	Viscosity*(25°C) (Centipoises)	Dielectric Constant(25°C)
0	100	2.52	64.6
20	80	2.52	69.1
40	60	2.52	74.6
60	40	2.52	80.5
80	20	2.55	87.2
100	0	Solid	Solid

* Determined Experimentally.

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS

* * * * * * *

Notes: 1) All tests were made in a dry argon atmosphere.

2) All solutions are saturated at less than one-molal unless marked otherwise.

3) All percentages are in weight basis.

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
a. Acetonitrile				
Blank	3.48×10^{-6} (28°C)	---	---	---
* KPF_6	3.30×10^{-2} (27°C)	Clear	White	---
LiCl	4.67×10^{-4} (28°C)	Clear	White	---
* $(n\text{-}C_3H_7)_4NPF_6$ (tetra-n-propylammonium hexafluorophosphate)	3.36×10^{-2} (27°C)	Brown	---	---
b. Dimethyl Cyanamide				
$AlCl_3$	1.57×10^{-2} (28°C)	Clear	Small Amount Gray	---
* $(n\text{-}C_4H_9)_3SnCl$(liq.) (tri-n-butyltin chloride)	9.15×10^{-5} (29°C)	Clear	---	Miscible
$(C_6H_5)_3SnCl$ (triphenyltin chloride)	9.90×10^{-5} (29°C)	Clear	White	---
c. Dimethylformamide				
* $NaB(C_6H_5)_4$ (sodium tetraphenylboron)	7.78×10^{-3} (28°C)	Clear Tan	Small Amount Tan	---
$Na(CF_3COO)$ (sodium trifluoroacetate)	5.73×10^{-3} (28°C)	Clear	White	---
* $(n\text{-}C_4H_9)_3SnCl$(liq.) (tri-n-butyltin chloride)	1.97×10^{-4} (29°C)	Clear	---	Miscible
$(C_6H_5)_3SnCl$ (triphenyltin chloride)	1.77×10^{-4} (29°C)	---	---	---

* One molal solutions.

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
	d. Mesityl Oxide			
KPF_6	6.43×10^{-4} (27°C)	Yellow	White	---
LiCl	3.17×10^{-5} (27°C)	Yellow	White	---
$(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	1.68×10^{-3} (27°C)	Black	Black	---
	e. N-nitrosodimethylamine			
$KAsF_6$	2.29×10^{-2} (29°C)	Yellow	Slight Amount White	---
* KPF_6	2.10×10^{-2} (30°C)	Yellow	---	---
$NaSbF_6$	2.34×10^{-2} (29.5°C)	Yellow	White	---
* $O\langle CH_2CH_2 \rangle NH_2PF_6$ (morpholinium hexafluorophosphate)	2.73×10^{-2} (29.5°C)	Yellow	---	---
* $(n\text{-}C_3H_7)_4NPF_6$ (tetra-n-propylammonium hexafluorophosphate)	2.39×10^{-2} (27.5°C)	Brown	---	---
* $(n\text{-}C_4H_9)_2NH_2AsF_6$ (di-n-butylammonium hexafluoroarsenate)	2.74×10^{-2} (30.5°C)	Yellow	---	---
$(C_6H_5CH_2)N(CH_3)_3SbF_6$ (N-benzyl N,N,N-trimethylammonium hexafluoroantimonate)	2.08×10^{-2} (28°C)	Yellow	Slight Amount Brown	---

* One molal solutions.

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations: Solution	Solid	Others
f. Propylene Carbonate				
$KAsF_6$	8.80×10^{-3} (25°C)	Clear	White	---
$NaSbF_6$	7.26×10^{-3} (26.5°C)	Turbid	White	---
* $(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	9.70×10^{-3} (28+°C)	Cloudy	---	---
* $(n\text{-}C_3H_7)_4NPF_6$ (tetra-n-propylammonium hexafluorophosphate)	1.00×10^{-2} (29°C)	Clear Brown	---	---
$O\langle CH_2CH_2 \rangle NH_2PF_6$ (morpholinium hexafluorophosphate)	1.03×10^{-2} (26°C)	Clear	Slight Amount White	---
* $(C_6H_5CH_2)N(CH_3)_3SbF_6$ (N-benzyl N,N,N-trimethylammonium hexafluoroantimonate)	8.15×10^{-3} (25°C)	Yellow	---	---
g. 60% Propylene Carbonate + 40% Ethylene Carbonate				
KPF_6	9.78×10^{-3} (29°C)	Clear	Slight Amount White	---
$O\langle CH_2CH_2 \rangle NH_2PF_6$ (morpholinium hexafluorophosphate)	1.14×10^{-2} (26°C)	Clear	Slight Amount White	---
$(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	1.05×10^{-2} (26°C)	Gray	Black	---
h. 40% Propylene Carbonate + 60% Ethylene Carbonate				
KPF_6	1.06×10^{-2} (30°C)	Clear	Slight Amount White	---
$O\langle CH_2CH_2 \rangle NH_2PF_6$ (morpholinium hexafluorophosphate)	1.22×10^{-2} (26.5°C)	Clear	White	---
$(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	1.08×10^{-2} (26°C)	Gray	Black	---

* One molal solutions.

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations		
		Solution	Solid	Others
i. 20% Propylene Carbonate + 80% Ethylene Carbonate				
* $AlCl_3$	8.65×10^{-3} (27°C)	Brown	---	---
FeF_3	1.14×10^{-4} (27°C)	Turbid	White	---
$InCl_3$	3.49×10^{-3} (27°C)	Clear	Slight Amount White	---
$LiCl$	9.31×10^{-4} (26°C)	Turbid	White	---
$KAsF_6$	1.21×10^{-2} (25°C)	Clear	White	---
$K_3Cr(SCN)_6$	6.63×10^{-3} (27°C)	Purple	Purple	---
KPF_6	1.16×10^{-2} (29°C)	Clear	Slight Amount White	---
$NaB(C_6H_5)_4$ (sodium tetraphenylboron)	2.15×10^{-3} (27°C)	Clear	Slight Amount Brown	---
$NaSbF_6$	8.81×10^{-3} (26°C)	Clear	White	---
$Na(CF_3COO)$ (sodium trifluoroacetate)	1.38×10^{-3} (27°C)	Turbid	White	---
* $SbCl_3$	2.76×10^{-4} (27°C)	Clear	---	---
SbF_3	1.21×10^{-4} (30°C)	Clear	White	---
$[(C_4H_9)_2NH_2]_2SiF_6$ (di-n-butylammonium hexafluorosilicate	2.08×10^{-4} (27°C)	Clear	Slight Amount White	---
$O\langle^{CH_2CH_2}_{CH_2CH_2}\rangle NH_2PF_6$ (morpholinium hexafluorophosphate)	1.31×10^{-2} (25°C)	Clear	Slight Amount White	---
$(C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	1.12×10^{-2} (25°C)	Gray	Black	---
$(C_6H_5CH_2)N(CH_3)_3SbF_6$ (N-benzyl N,N,N-trimethylammonium hexafluoroantimonate)	9.85×10^{-3} (25°C)	Yellow	Slight Amount Black	---

* One molal solutions.

TABLE IV. SPECIFIC CONDUCTANCE OF SOLUTIONS (Continued)

Solute	Specific Conductance (ohm^{-1} cm^{-1})	Visual Observations: Solution	Solid	Others
j. 10% Propylene Carbonate + 90% Ethylene Carbonate				
KPF_6	1.22×10^{-2} (30°C)	Clear	Slight Amount White	---
k. N,N,N',N' Tetramethyldiaminomethane				
KPF_6	1.37×10^{-9} (27°C)	Clear	White	---
$(n\text{-}C_3H_7)_4NBF_4$ (tetra-n-propylammonium tetrafluoroborate)	3.08×10^{-9} (27°C)	Clear	White	---
$(n\text{-}C_3H_7)_3NHAsF_6$ (tri-n-propylammonium hexafluoroarsenate)	2.68×10^{-9} (27°C)	Clear	White	---
LiCl	1.48×10^{-9} (28°C)	Clear	White	---
l. N,N,N',N' Tetramethylethylenediamine				
KPF_6	2.42×10^{-8} (28°C)	Clear	White	---
$(n\text{-}C_3H_7)_4NBF_4$ (tetra-n-propylammonium tetrafluoroborate)	1.18×10^{-8} (27°C)	Clear	White	---
$(n\text{-}C_3H_7)_3NHAsF_6$ (tri-n-propylammonium hexafluoroarsenate)	1.45×10^{-8} (27°C)	Clear	White	---
LiCl	1.37×10^{-8} (28°C)	Clear	White	---
m. Trifluoroacetic Anhydride				
KPF_6	8.13×10^{-8} (27°C)	Clear	White	---
LiCl	3.92×10^{-8} (27°C)	Clear	White	Gas Evolution
$C_6H_5)N(CH_3)_3PF_6$ (N-phenyl N,N,N-trimethylammonium hexafluorophosphate)	4.46×10^{-6} (27°C)	Clear	White	---

TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS

* No viscosity data are available for these solutions.

TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS

a. KPF_6-Dimethyl Cyanamide

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0	---	0.670	0.883
0.0878	0.695×10^{-2} (24°C)	0.750	0.894
0.260	0.917×10^{-2} (24°C)	0.809	0.915
0.427	1.17×10^{-2} (24°C)	0.935	0.933
0.595	1.34×10^{-2} (24°C)	1.050	0.955
* 0.828	1.49×10^{-2} (24°C)	1.258	0.981

* Solid present.

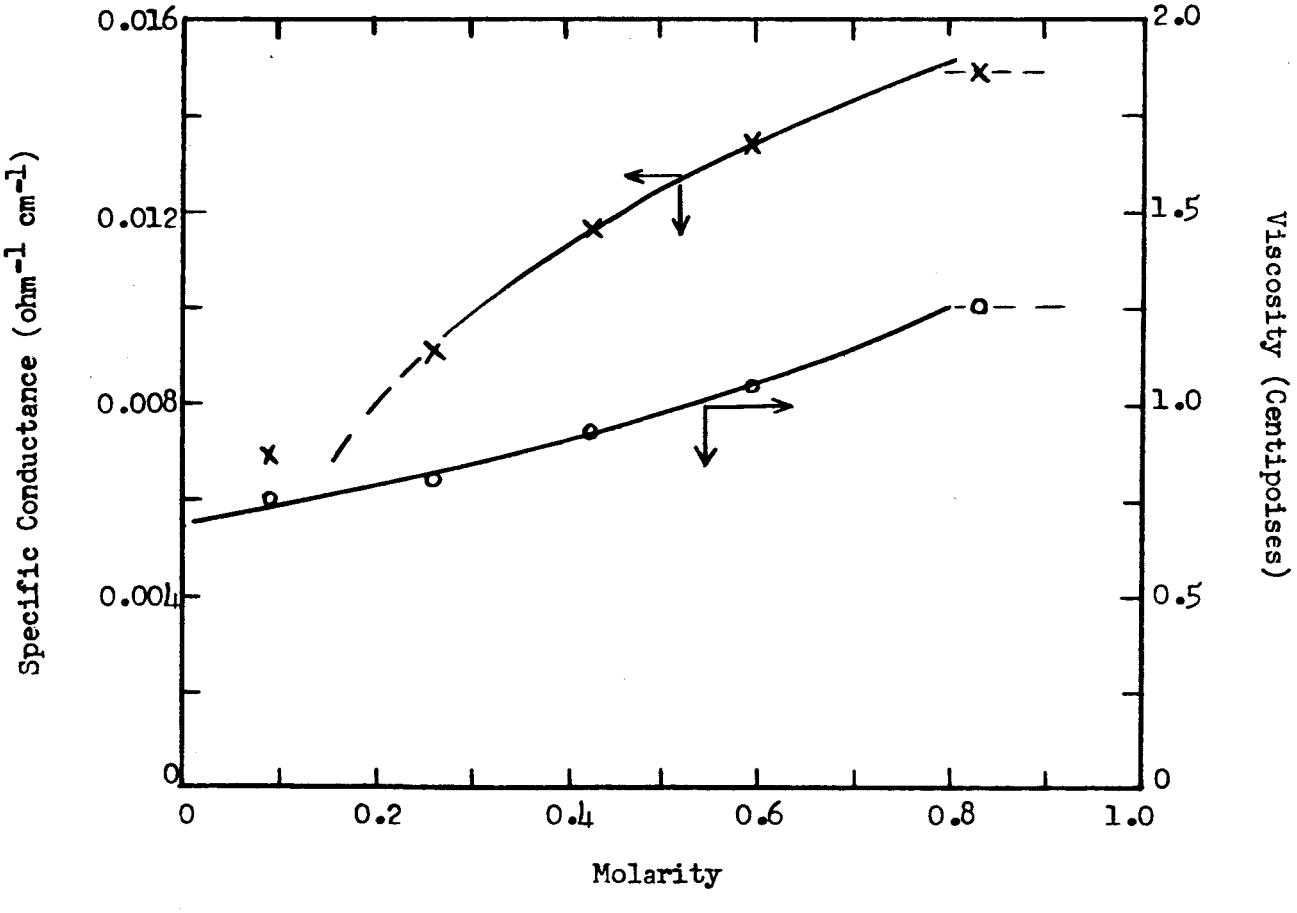


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

b. $NaSbF_6$-Dimethyl Cyanamide

Molality	Specific Conductance (ohm^{-1} cm^{-1})
0.441	1.50×10^{-2} (26.5°C)
0.883	2.10×10^{-2} (26.5°C)
1.325 (Solid Present)	2.29×10^{-2} (26.5°C)
1.46 (Solid Present)	2.29×10^{-2} (26.5°C)
1.765 (Solid Present)	2.23×10^{-2} (26.5°C)
2.210 (Solid Present)	2.11×10^{-2} (26.5°C)

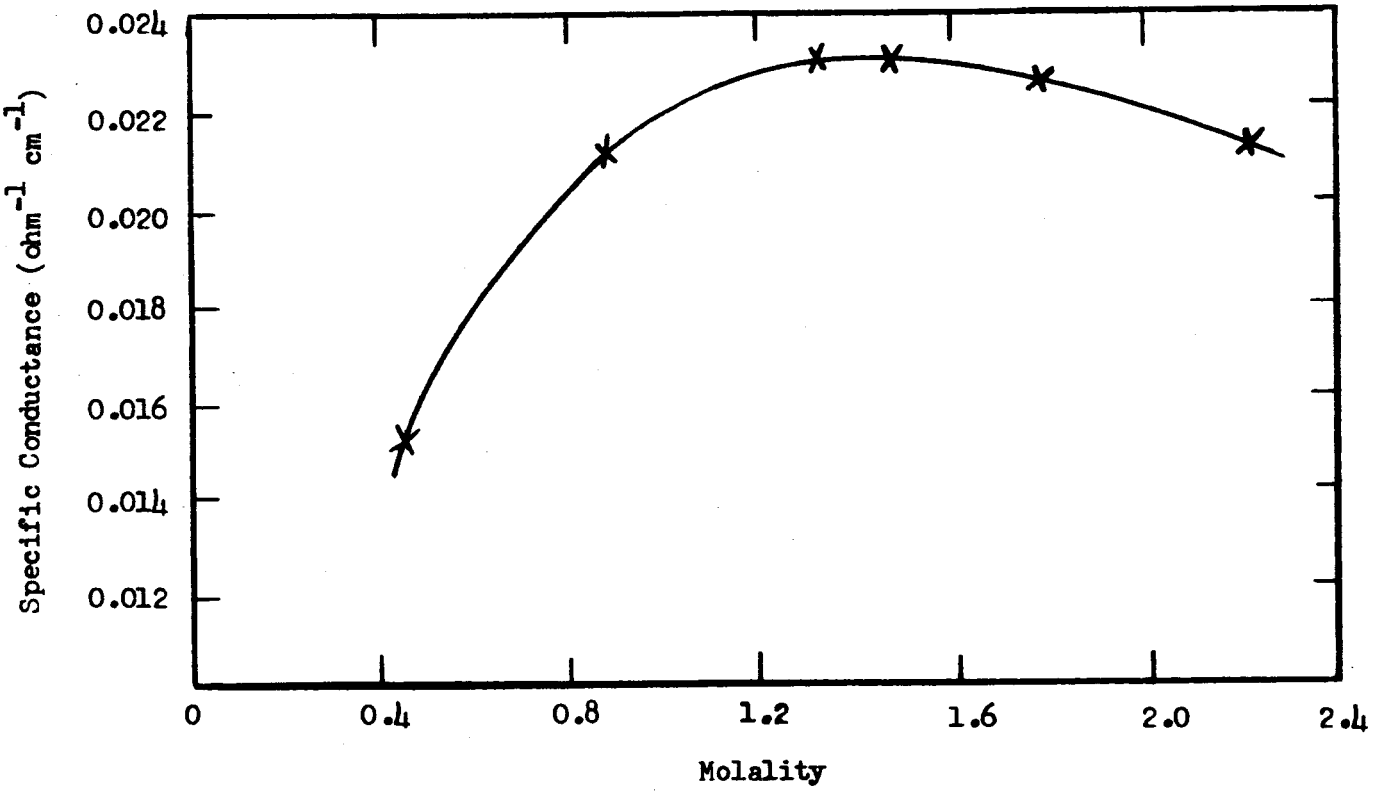


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

c. $(n\text{-}C_3H_7)_4NPF_6$-Dimethyl Cyanamide

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0.248	1.20×10^{-2} (25°C)	0.808	0.907
0.397	1.615×10^{-2} (25°C)	0.914	0.920
0.718	2.12×10^{-2} (25°C)	1.205	0.952
0.976	---	1.615	0.9755
1.29	2.10×10^{-2} (25°C)	2.24	1.007
1.39	2.02×10^{-2} (25°C)	2.51	1.016
1.55	1.81×10^{-2} (25°C)	----	* 1.032

* Extrapolated value.

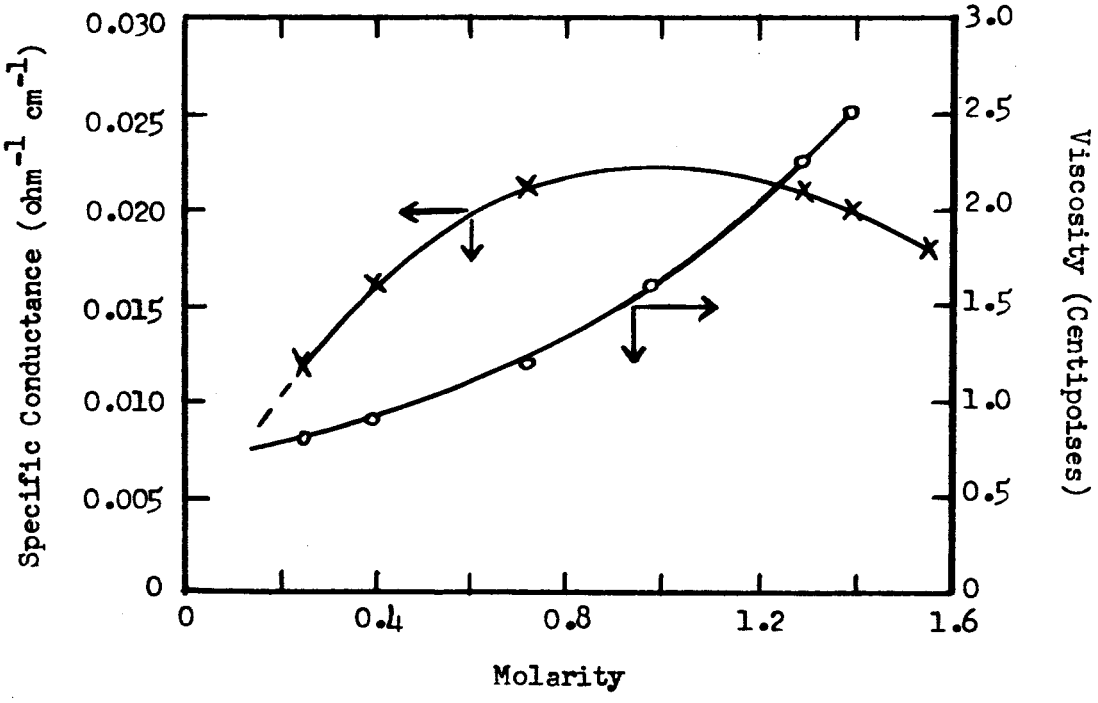


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

d. $K_3Cr(SCN)_6$-Dimethylformamide

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0	---	---	0.945
0.221	1.43×10^{-2} (31°C)	1.92	1.009
0.417	1.505×10^{-2} (30°C)	3.53	1.026
0.606	1.18×10^{-2} (32°C)	10.8	1.101
0.758	8.47×10^{-3} (30°C)	---	* 1.151

* Extrapolated value.

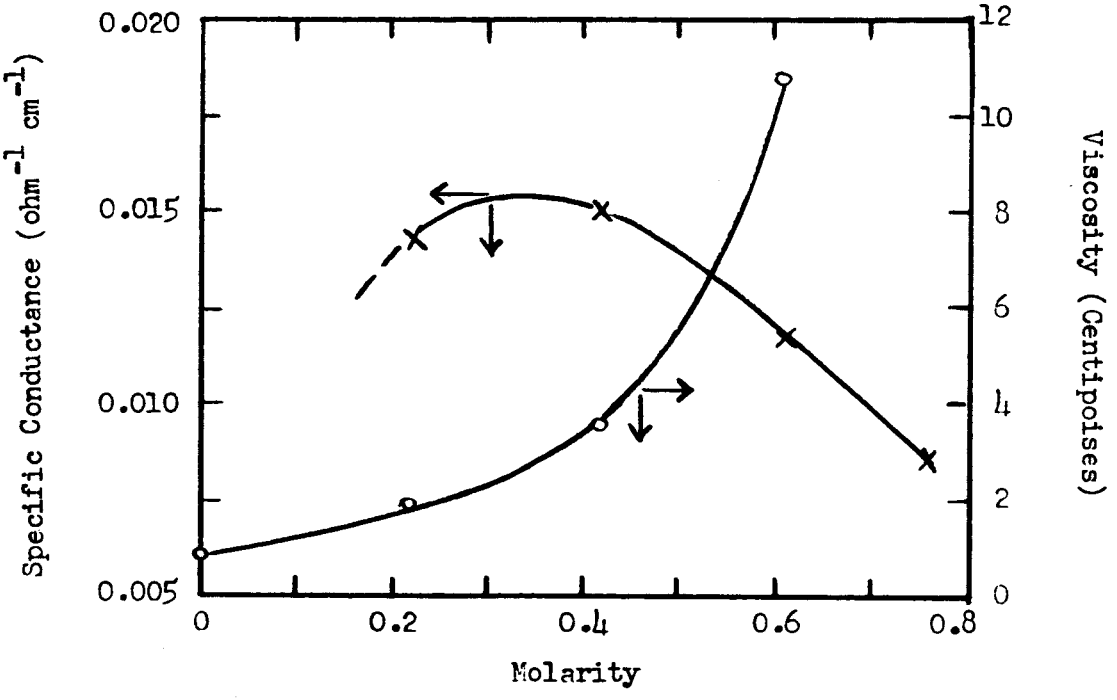


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

e. $NaB(C_6H_5)_4$-Dimethylformamide

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0.723	7.78×10^{-3} (28°C)	---	* 0.972
0.836	7.86×10^{-3} (29°C)	---	* 0.982
0.896	---	5.40	0.991
0.947	6.33×10^{-3} (28°C)	---	* 1.000
1.074	5.68×10^{-3} (29°C)	6.90	1.025
1.28	3.28×10^{-3} (30°C)	---	** ≈1.08

* Interpolated value.
** Extrapolated value.

TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

f. $NaSbF_6$-Dimethylformamide

Molality	Specific Conductance (ohm^{-1} cm^{-1})
0.41	1.50×10^{-2} (27°C)
0.82	2.12×10^{-2} (27°C)
1.23	2.24×10^{-2} (27°C)
1.64	2.12×10^{-2} (27°C)
2.05	1.78×10^{-2} (27°C)

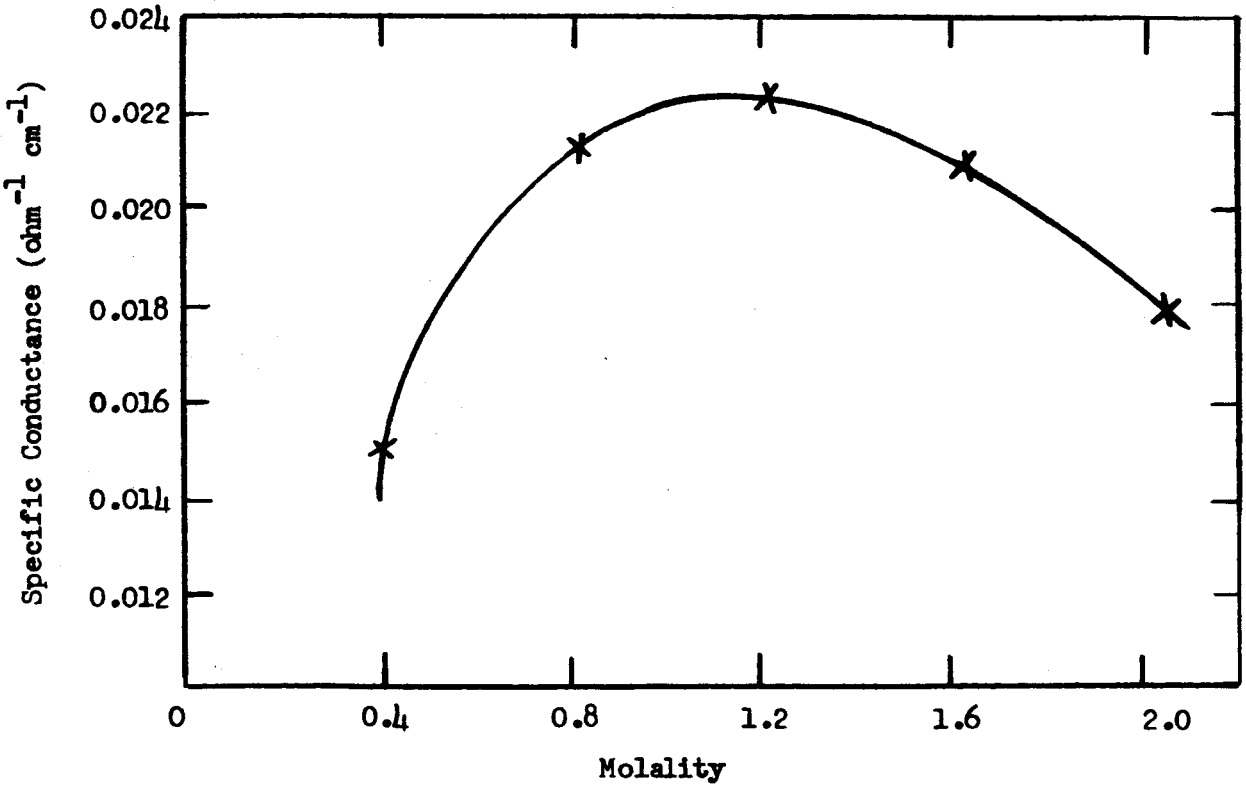


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

g. KPF_6-Nitrosodimethylamine

Molality		Specific Conductance (ohm^{-1} cm^{-1})
0.199		1.05×10^{-2} (31°C)
0.398		1.51×10^{-2} (30°C)
0.580		1.83×10^{-2} (30°C)
0.796		2.00×10^{-2} (30°C)
0.995		2.10×10^{-2} (30°C)
1.195	(Solid Present)	2.14×10^{-2} (30°C)
1.39	(Solid Present)	2.14×10^{-2} (30°C)
1.99	(Solid Present)	2.15×10^{-2} (31°C)

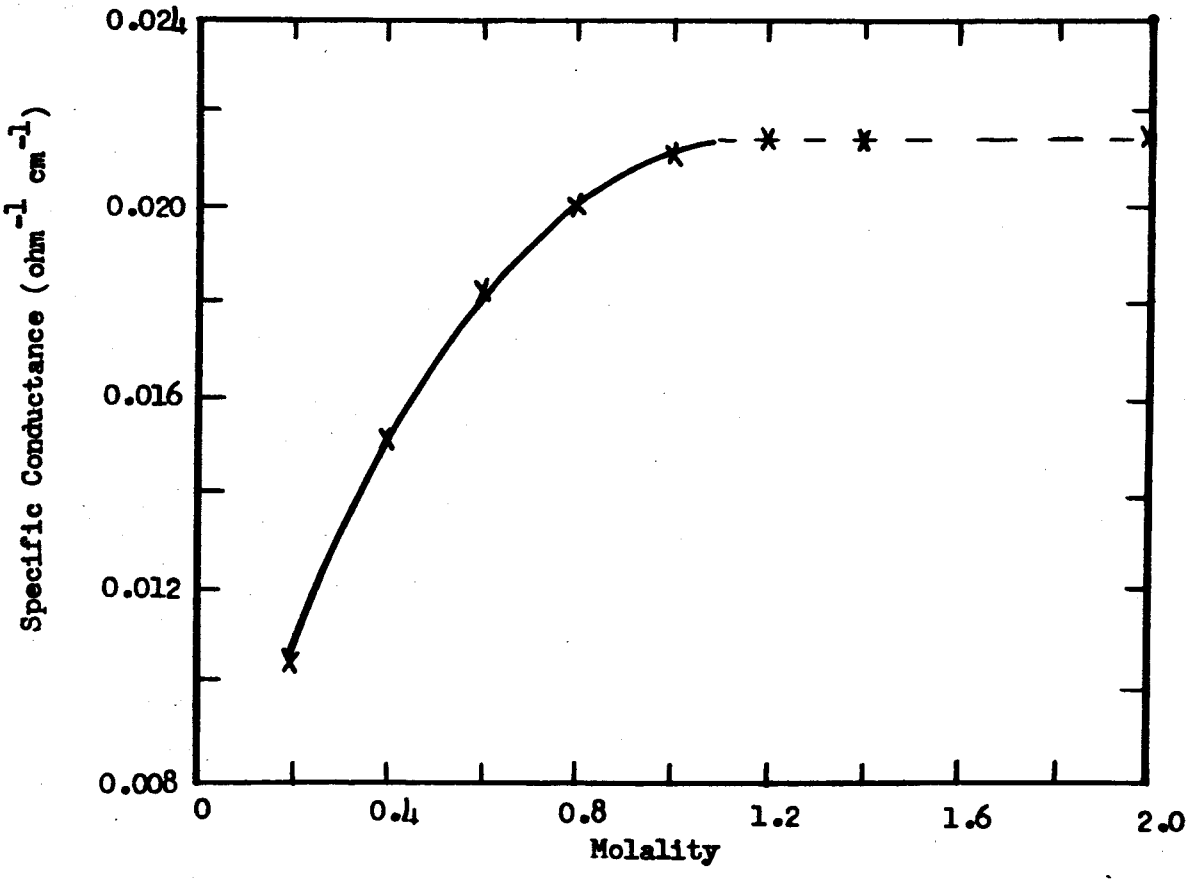


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

h. Morpholinium Hexafluorophosphate-Nitrosodimethylamine

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0.210	1.16×10^{-2} (31°C)	0.946	1.025
0.408	1.82×10^{-2} (31°C)	1.08	1.043
0.597	2.26×10^{-2} (31°C)	1.245	1.064
0.774	2.60×10^{-2} (30°C)	1.390	1.080
0.943	2.72×10^{-2} (30°C)	1.560	1.096
1.100	2.65×10^{-2} (30°C)	1.750	1.111
1.255	2.73×10^{-2} (29°C)	---	* 1.130
1.59	2.69×10^{-2} (29°C)	2.720	1.162

* Interpolated value.

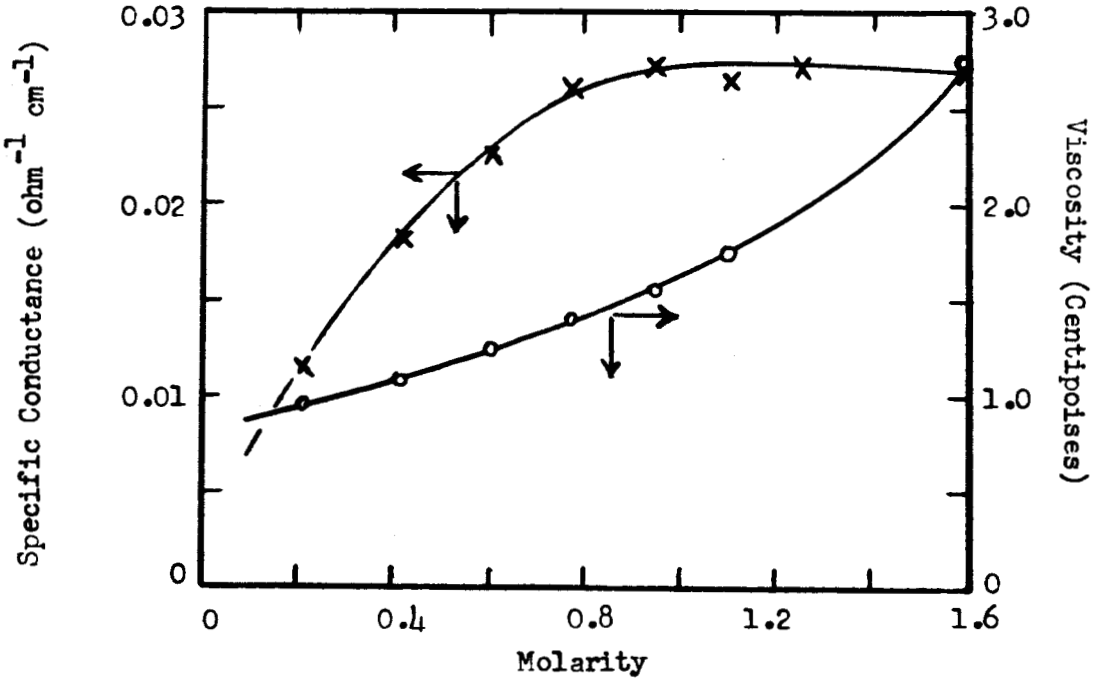


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

i. $(n\text{-}C_4H_9)_2NH_2AsF_6$-Nitrosodimethylamine

Molality	Specific Conductance (ohm^{-1} cm^{-1})
0.209	1.135×10^{-2} (31°C)
0.418	1.88×10^{-2} (31°C)
0.626	2.31×10^{-2} (31°C)
0.835	2.57×10^{-2} (30.5°C)
1.045	2.74×10^{-2} (30.5°C)
1.25	2.79×10^{-2} (30.5°C)
1.46	2.79×10^{-2} (31°C)
1.67	2.77×10^{-2} (31°C)
1.88	2.71×10^{-2} (30.5°C)
2.09	2.62×10^{-2} (31°C)

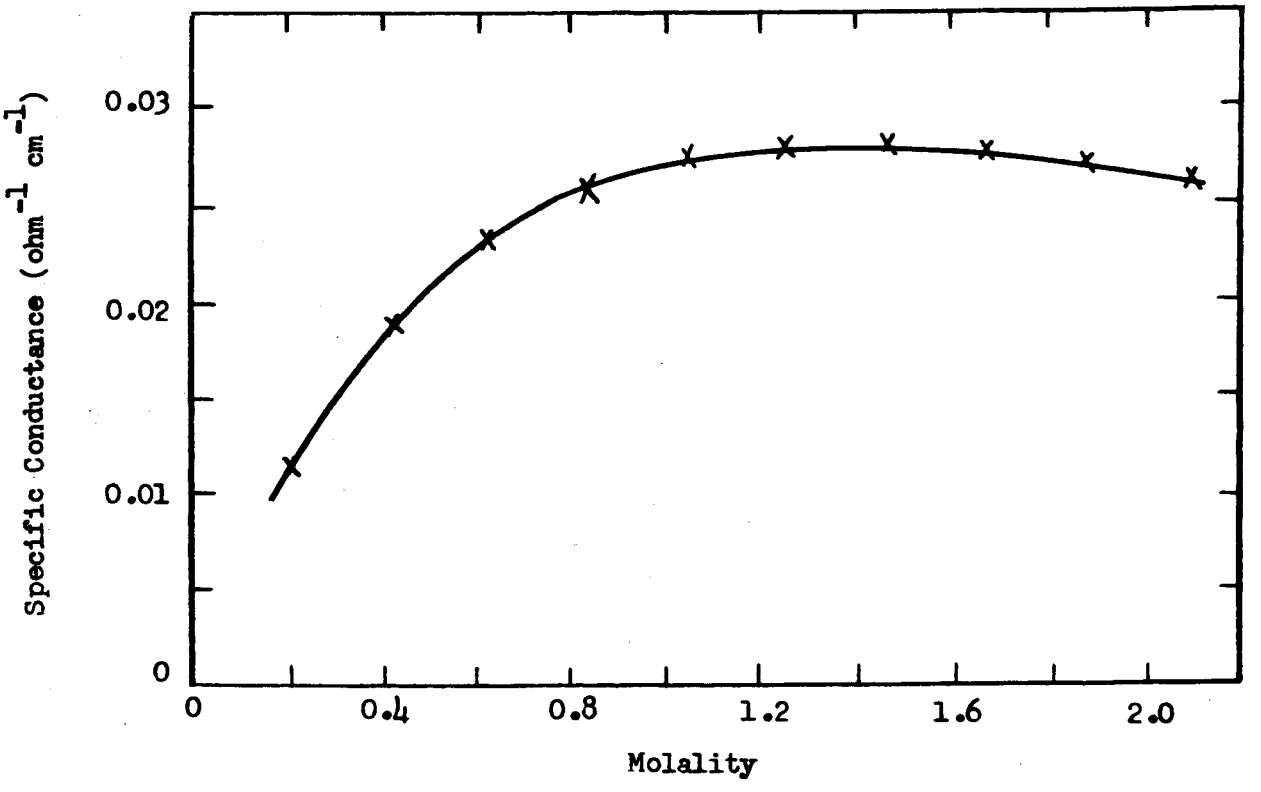


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

j. $AlCl_3$-(80% Ethylene Carbonate + 20% Propylene Carbonate)

Molality	Specific Conductance (ohm^{-1} cm^{-1})
0.297	4.46×10^{-3} (28°C)
0.70	7.85×10^{-3} (27.5°C)
0.987	8.63×10^{-3} (27°C)
1.295	9.03×10^{-3} (28°C)
1.72	8.34×10^{-3} (28°C)
2.01	7.08×10^{-3} (27°C)

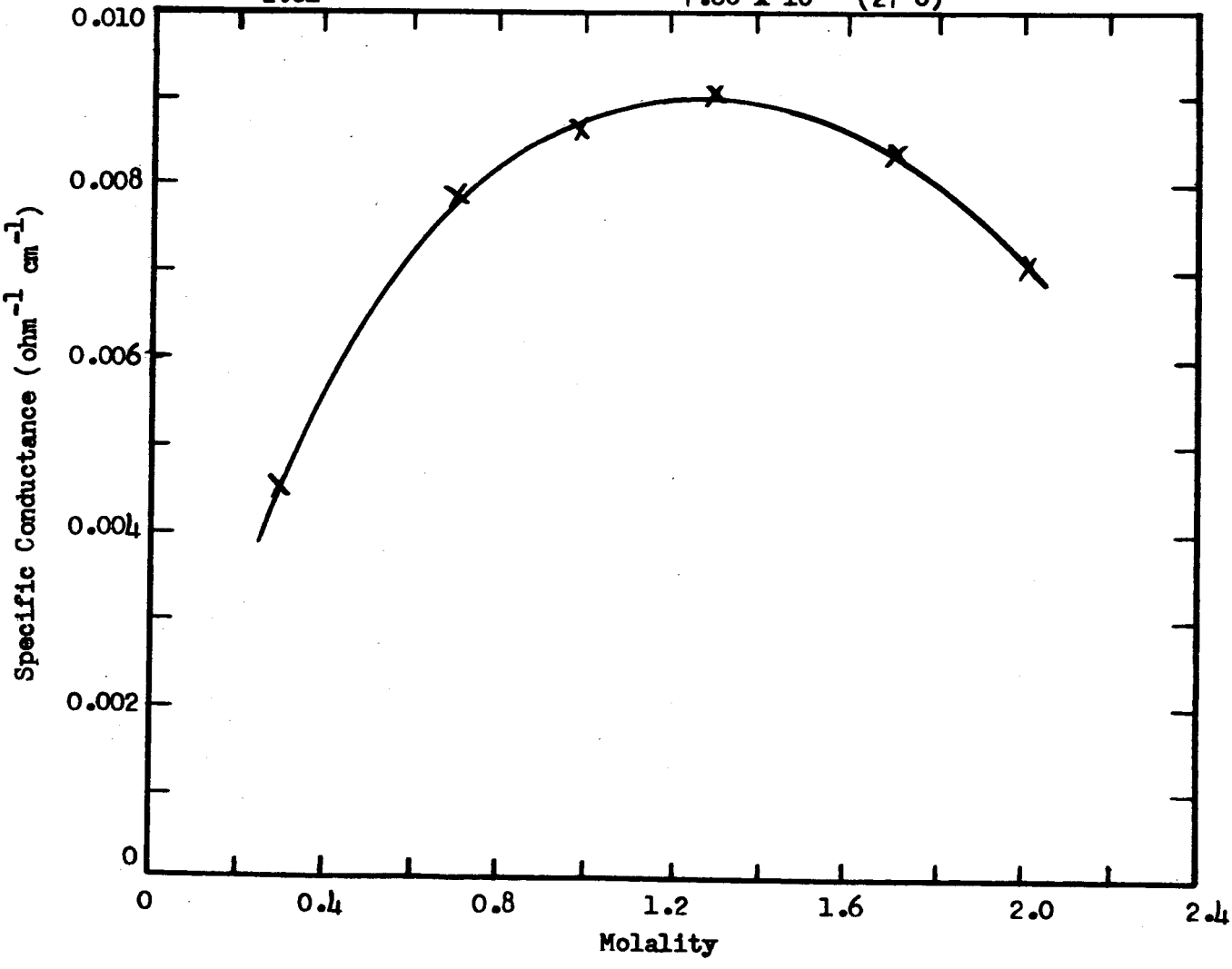


TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

k. $KAsF_6$-(80% Ethylene Carbonate + 20% Propylene Carbonate)

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0.383	0.72×10^{-2} (27°C)	3.32	1.357
0.743	1.07×10^{-2} (27°C)	4.29	1.402
1.08	1.10×10^{-2} (27°C)	5.26	1.442
1.405	1.28×10^{-2} (27°C)	6.78	1.488

Note: Solid present in every sample.

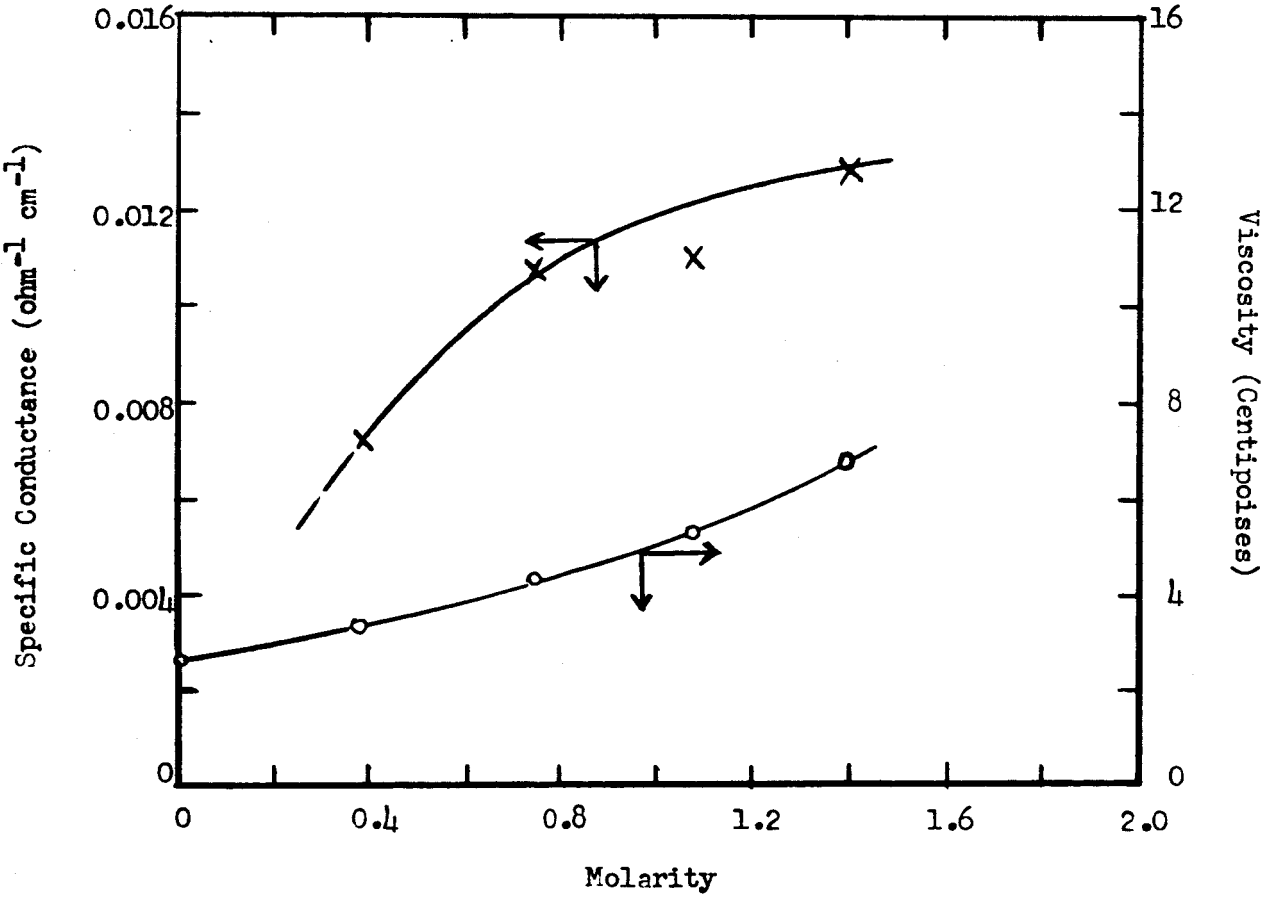


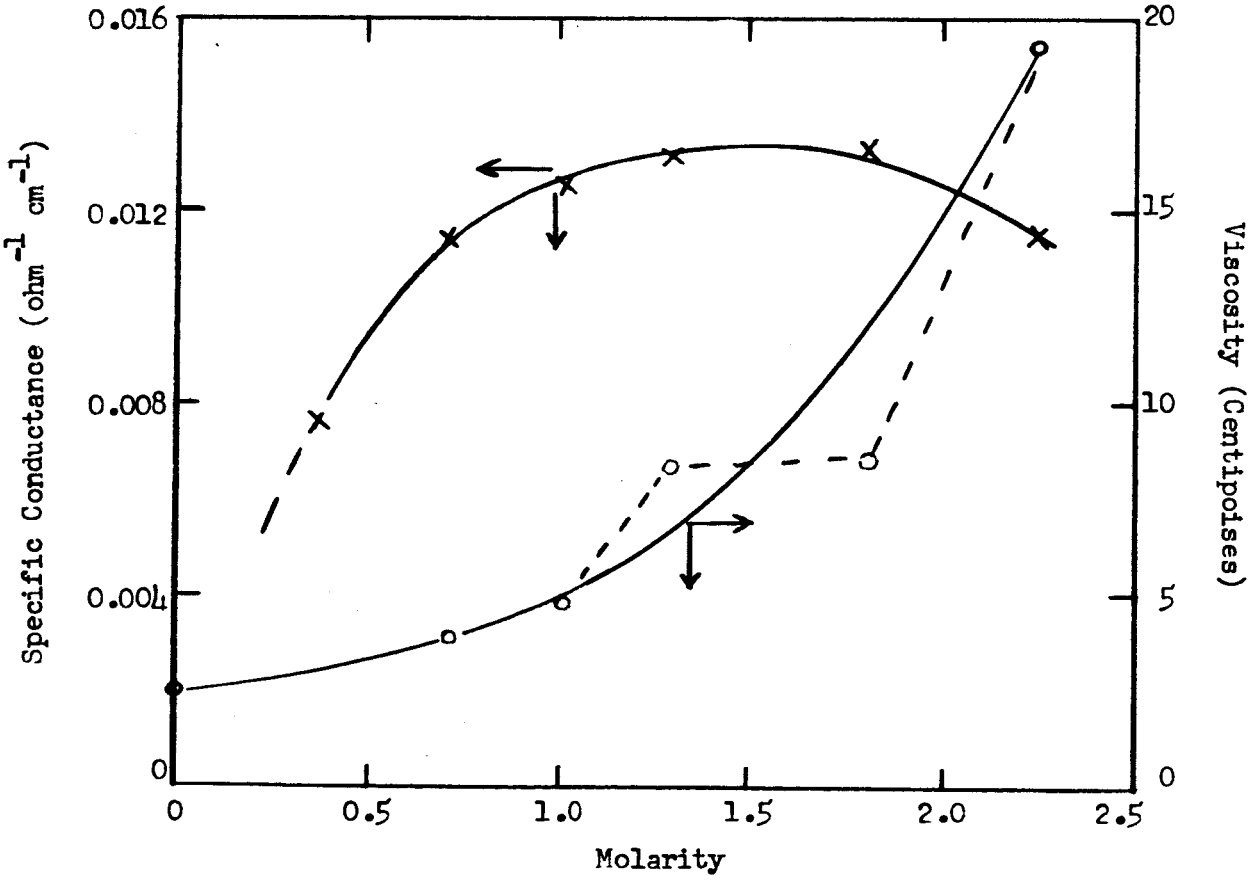
TABLE V. SPECIFIC CONDUCTANCE AND VISCOSITY VS. CONCENTRATION OF SOLUTIONS (Continued)

1. Morpholinium Hexafluorophosphate-(80% Ethylene Carbonate + 20% Propylene Carbonate)

Molarity (25°C)	Specific Conductance (ohm^{-1} cm^{-1})	Viscosity(25°C) (Centipoises)	Density (25°C)
0.372	0.759×10^{-2} (28°C)	---	* 1.328
0.710	1.14×10^{-2} (28°C)	3.88	1.349
1.015	1.25×10^{-2} (28°C)	4.75	1.367
1.30	1.315×10^{-2} (28°C)	8.38	1.408
1.805	1.33×10^{-2} (28°C)	8.53	1.407
2.25	1.15×10^{-2} (28°C)	19.3	1.460

* Interpolated value.

Note: Solid present in every sample.



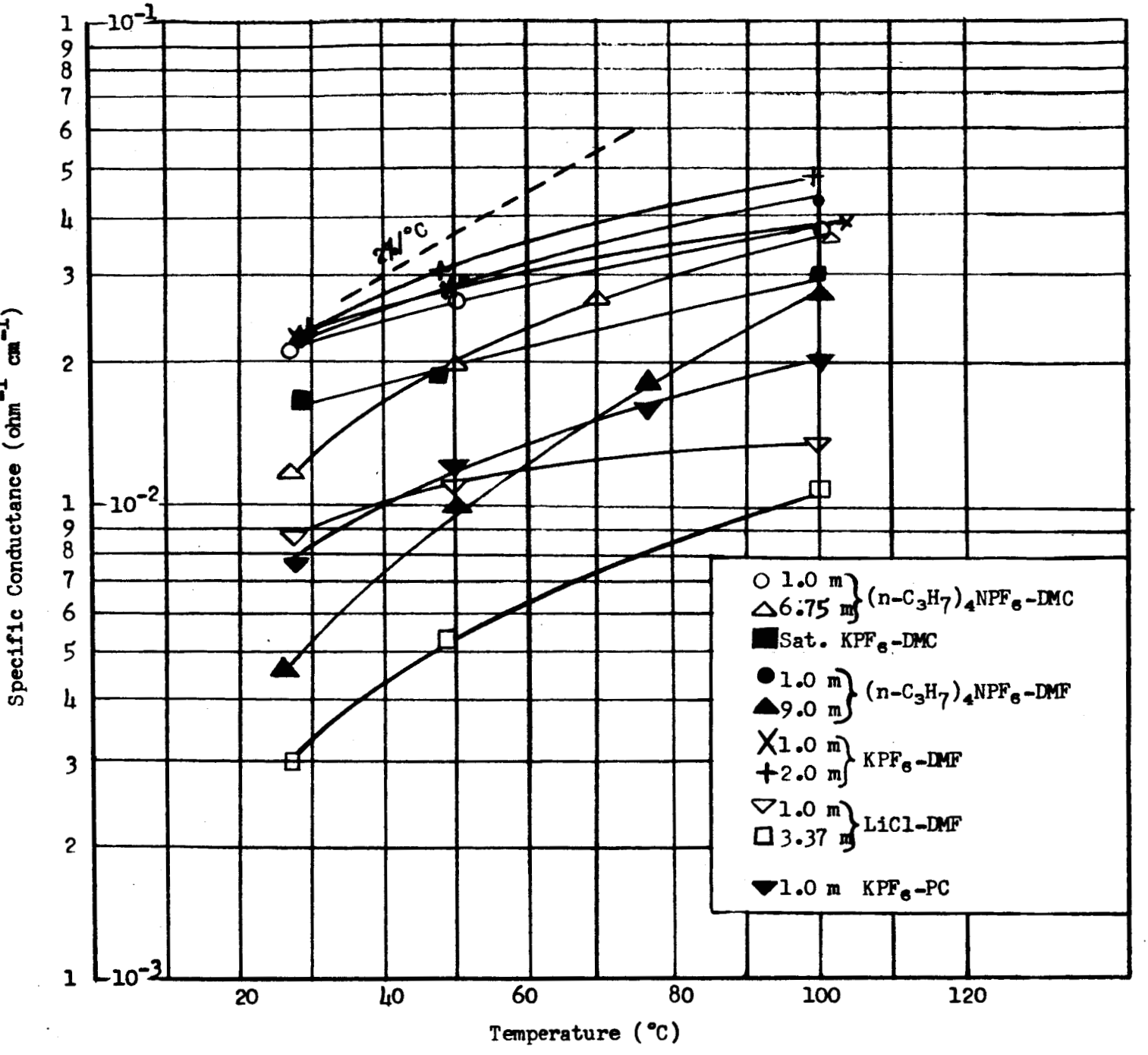
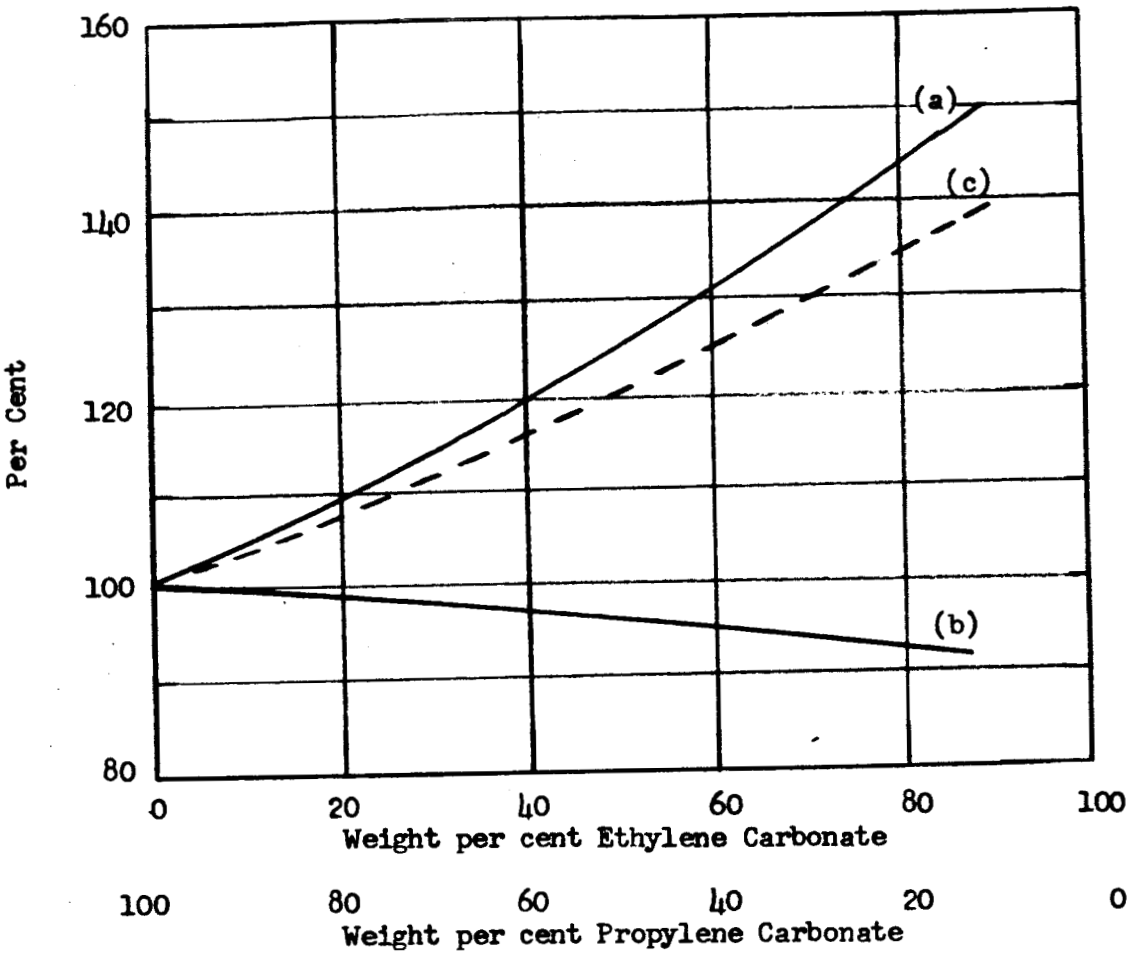


FIGURE 1. SPECIFIC CONDUCTANCE OF SOLUTIONS VS. TEMPERATURE



Curves:

(a) Specific conductances (29-30°C) of one-molal KPF_6.

(b) Viscosities (25°C) of one-molal KPF_6.

(c) Dielectric constants (25°C) of solvent.

100% Values (one-molal KPF_6-PC):

Specific conductance = 8.10×10^{-3} ohm^{-1} cm^{-1} at 29°C.

Viscosity = 6.25 centipoises at 25°C.

FIGURE 2. PROPERTIES OF KPF_6 SOLUTIONS VS. EC-PC SOLVENT COMPOSITION

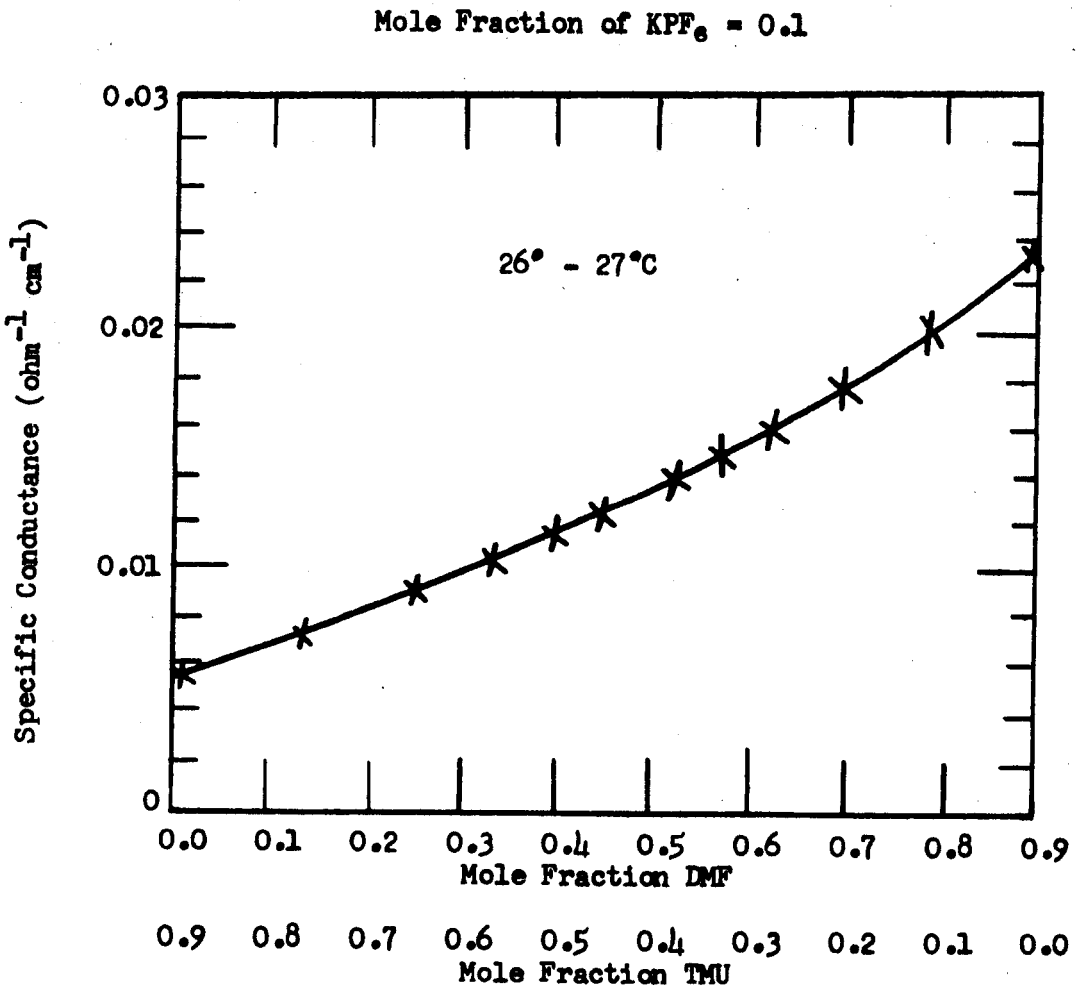


FIGURE 3. SPECIFIC CONDUCTANCE OF KPF_6-DMF-TMU SOLUTIONS

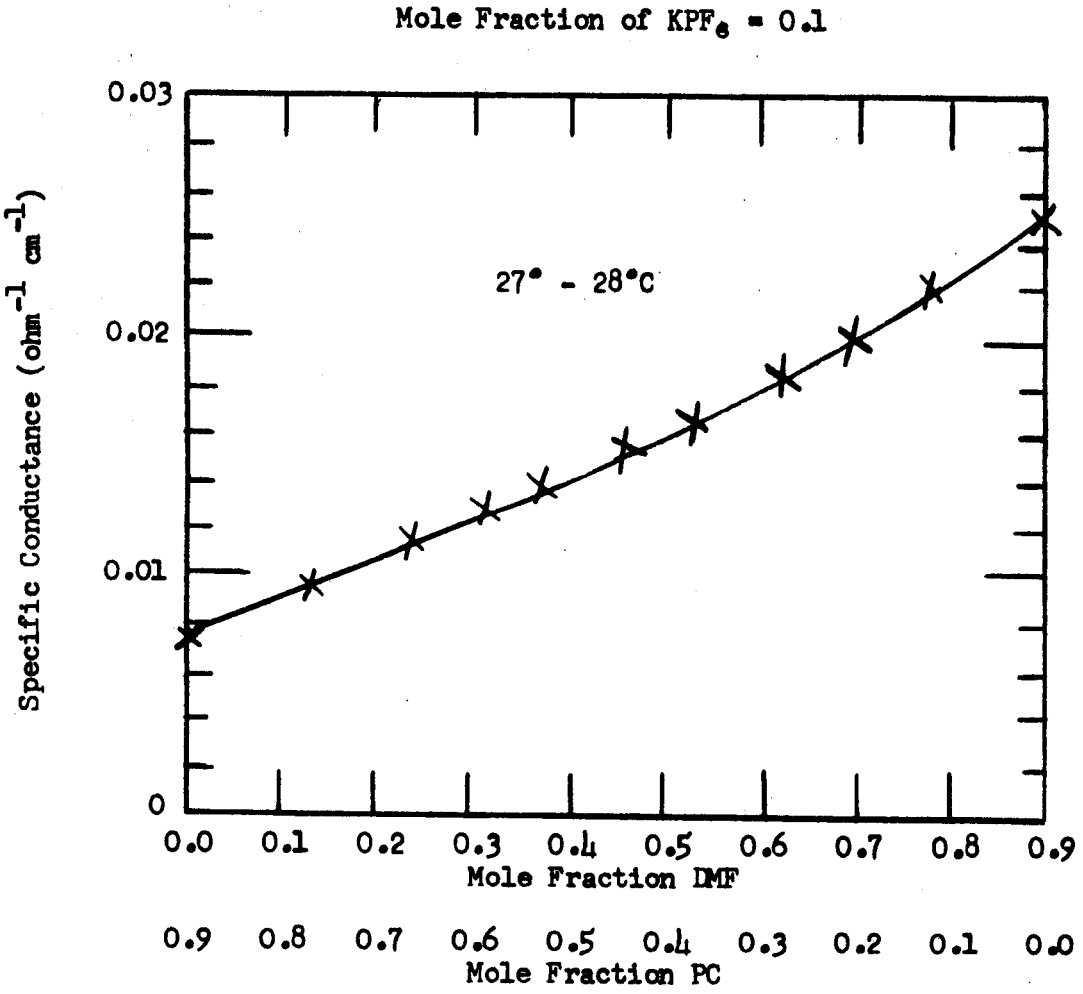


FIGURE 4. SPECIFIC CONDUCTANCE OF KPF_6-DMF-PC SOLUTIONS

V. APPENDIX I

V. APPENDIX I

Importance of Methods of Expressing Concentration in Conductance Studies

The mode of expressing concentration (i.e. as molal, normal, or molar) is highly important in the correct and reliable comparison of the data from one electrolyte system to another. Therefore, we present here a brief discussion of the differences between the methods of expressing concentration as related to conductance.

For screening purposes, the primary interest is in the magnitude of the specific conductance. Finding solutions with the highest values of conductance is more important than the mode of expressing concentration. Even in quantitative work the solution with the highest maximum specific conductance is most important. Expression of concentration in molality is satisfactory in these cases since it adequately performs the function of defining the system.

However, whenever the direct comparison of the efficiency of performance of the solutes in different systems is necessary, it is dangerous to compare different systems of the same molality. Since conductance is the current-carrying capacity of a liquid between two fixed points or areas, it is concerned with a fixed volume of the liquid. And since the population of ionizable solute determines the maximum achievable level of current carriers, a critical performance comparison between electrolytes should

be made on the basis of ionizable solute concentration per unit volume. However, different one-molal systems do not necessarily contain the same number of solute molecules per unit volume. It is therefore necessary to convert to an expression of concentration in terms of the same normality or molarity before comparing systems. It is then possible to determine which of two or more solutes or solutions exhibits the most effective utilization of the dissolved solute. The discussion below will amplify these statements.

The specific conductance of solutions is measured in conductance cells which possess a constant volume between the two electrodes at a given temperature. Thus, the conductance is determined by the number, charge, and mobility of the ions in the constant volume between the electrodes. When it is necessary to make reliable comparisons of the conductances of different solutions, the volume of solution between the electrodes must contain an amount of solute which, if completely dissociated, would produce the same number of ionic charges per unit volume for each of the solutions being compared. The method of expressing concentration which would express the same concentration of potential charge carries per unit volume is the normal solution (gram-equivalents per liter of solution). For a 1:1 electrolyte the same equivalence would be observed for a molar solution (gram moles per liter of solution). It should be remembered that both normal and molar solutions are temperature dependent because of volume changes with temperature and precise comparisons thus require rigid temperature control.

Experimentally, where we seek a quick determination of the maximum conductivity, it is simplest to add incremental amounts of solute to a given amount of solvent and measure the conductivity at each concentration achieved. We can define each system adequately for purposes of reproduction by expressing concentration as gram moles of solute per 1000 grams of solvent -- i.e., in molality. To convert to molarity for comparison as described above, the density of each solution must also be measured. Then the conversion from molality to normality can be made with the following equation:

(1) $$C_N = \frac{n\, m\, \rho}{1 + \frac{(M.W.)m}{1000}}$$

Where C_N = normality (gram-equivalents/liter of solution)

n = number of gram equivalents/mole of solute

m = concentration in molality

ρ = density of the solution in g./ml.

M.W. = gram molecular weight of the solute

The conversion from molality to molarity can be obtained with a similar equation:

(2) $$C_M = \frac{m\, \rho}{1 + \frac{(M.W.)m}{1000}}$$

Where C_M = molarity

and all other symbols have the same meaning as in equation (1).